Roll-to-roll CZTS from ab initio thermodynamics

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Global photovoltaic (PV) electricity generation is currently of the order 7GW, while global energy consumption (including liquid fuels) is of the order 15TW. In order to make a significant contribution to the energy mixture, PV generation must be hugely expanded. Ultimately, "country-sized" schemes are needed.[1] A useful approach to raise the application of PV by orders of magnitude is building-scale functional coatings. This aligns with the interests of building cladding manufacturers, including Tata Steel and NSG, which are backing the SPECIFIC consortium to develop building-integrated technologies. Abundant thin-film absorbers such as Cu_2ZnSnS_4 (CZTS) are attractive for providing PV. However, scalable roll-to-roll processes are far-removed from laboratory prototypes.

Roll-to-roll considerations

A number of synthesis routes have been identified, but whether the precursors are binary compounds, salts in solution, metal alloys or pre-formed CZTS nanoparticles, film formation typically takes place in a high-temperature annealing process with sulfur vapour. This critical step involves complex phase equilibria and is suited to a thermodynamic study. In roll-to-roll processing, annealing must be kept as rapid as possible in order to support a continuous production line. It is also difficult to supply pressures which are far-removed from ambient.

Near-infrared (NIR) heating is of particular interest, and has already been applied to rapid sintering of TiO2 for dye-sensitised cells.[2] The use of H_2S in some CZTS preparations is also of concern; while it is employed as an industrial gas in some contexts it would be difficult to adequately contain such a toxic material on a roll-to-roll conveyer system.

Pilot-scale roll-to-roll facilities at the SPECIFIC R&D site

Computational details

The University of Bath's 800-core Aquila cluster is used for structure optimisation and testing: demanding phonon calculations are carried out on national-scale facilities (The Cray XE6 system "HECToR", via the EPSRC and MCC, and the STFC's Bluegene/Q system "Blue Joule").

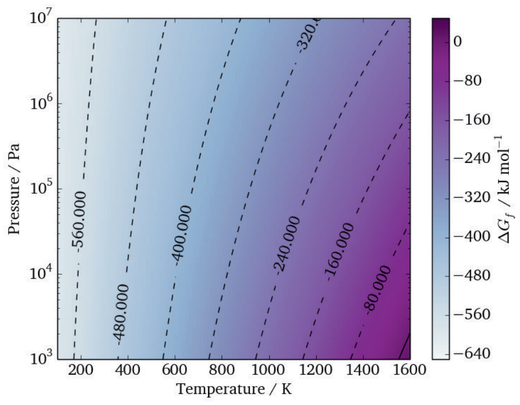
Calculations are primarily carried out using the FHI-aims quantum chemistry code with the PBEsol functional for exchange and correlation . This offers a balance of efficiency and accuracy, while being readily scalable across thousands of computing cores.

Phonon calculations are set up and processed with the "Phonopy" package, and thermodynamic modelling is executed with Scientific Python and Matlab.

While this aspect of the work is theoretical, the results are tied to a wider UK experimental programme at Bath, Bristol and Northumberland.

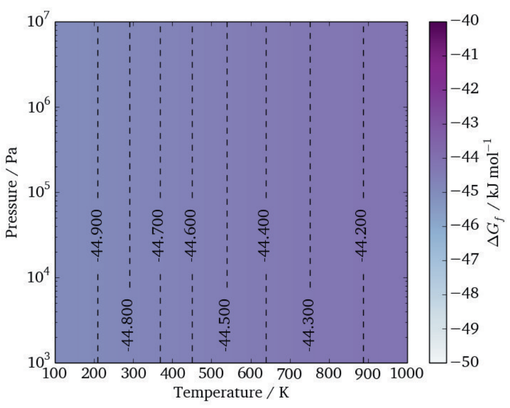
Free energy surfaces

A chief difficulty in the development of viable CZTS coatings is the complex phase diagram, which includes binary and ternary phases as well as stabililising defects.[3]



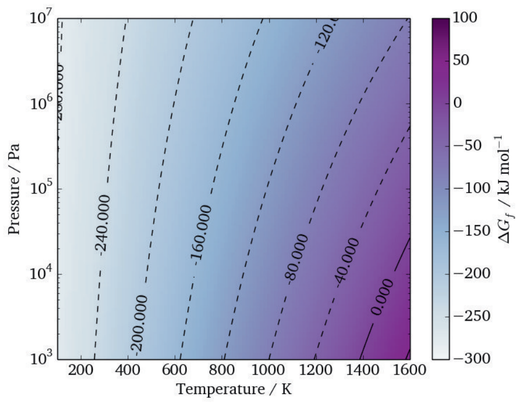
Formation free energy surface for CZTS

$2Cu + Zn + Sn + 2S_2 \rightarrow CZTS$



Free energy surface for CZTS relative to binaries

$Cu_2S + ZnS + SnS_2 \rightarrow CZTS$



Formation free energy surface allowing decomposition to Sn

$Cu_2S + ZnS + Sn + 2S_2 \rightarrow CZTS$

Phase equilibria are explored by examining the free energy surfaces of hypothetical reactions. Once free data is available, interactions can be modelled rapidly. At this stage, the elemental components and simple binary compounds have been modelled. Future work will introduce more compounds and more sophisticated gas-phase modelling.

Ab initio thermodynamics

The structures and energies of moderately complex crystalline materials (~100 atoms in a unit cell) may be studied with some confidence using density functional theory (DFT). These methods typically model an athermal ground state; this is not representative of typical usage conditions, and lies even further from industrial reaction conditions.

Temperature and pressure effects can be introduced by calculating key bulk properties including the heat capacity and vibrational entropy. By using this data to construct the chemical potential (μ) for each compound of interest, the Gibbs free energy (ΔG) may be calculated for arbitrary reactions and conditions:

$$\Delta G = \sum_i \mu_i$$

$$\mu = E_{\mathrm{DFT}} + E_{\text{zero-point}} + \int_0^T C_p \mathrm{d}T + PV - TS$$

In the solid state, full phonon spectra may be computed from a series of structures with small displacements to form a set of approximate harmonic normal modes. By filling these modes according to the Boltzmann distribution, free energies can be calculated. Industrial gases are largely well-described in the literature; the challenge lies in bringing the data together to form a consistent model of gas-vapour equilibrium.

[1] MacKay, D. J. C. *Philos Trans. R. Soc. A.* **2013**, *371*, 20110431

[2] Watson, T.; Mabbett, H.; Wang, H.; Peter, L; Worsley, D. *Prog Photovoltaics* **2011**, *19*, 482

[3] Chen, S.; Gong, X. G.; Walsh, A.; Wei, S. *Appl. Phys. Lett.* **2010**, *96*, 021902

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